

Performance Monitoring Protocol (QA/QC) for the Pyrolysis-GC/MS (Py-GC/MS)

1 Scope

This document addresses the performance monitoring (QA/QC) of a GC/MS (EI) with a pyrolysis autosampler. This document applies to personnel using the associated instrument(s)/equipment in Quantico, VA in the following disciplines/categories of testing: Paint and Chemistry Unit general physical and chemical analysis.

2 Principle

The pyrolysis-GC/MS system consists of a Gas Chromatograph (GC) with a single quadrupole Mass Selective Detector (MSD) and a pyrolysis autosampler. The instrument is configured with a dedicated electron impact ionization (EI) source. It may also be referred to as a 'Py-MSD.' Definitions and guidelines for following this protocol are outlined in the "General Instrument Maintenance Protocol."

Pyrolysis is a technique used to break chemical bonds using in macromolecules using thermal energy. The pyrolysis products, known as pyrolyzates, are introduced onto the GC column by the carrier gas through a heated transfer line. The elution order of the pyrolyzates by gas chromatography and the structural information ascertained from the observed fragmentation pattern of each can be used to identify the pyrolyzates present.

3 Equipment/Materials/Reagents

- a. Instrumentation - Gas Chromatograph, Mass Selective Detector with EI Source, and Software (Agilent or equivalent)
- b. Autosampler - Pyrolysis Autosampler, accessories, and software (Frontier, or equivalent)
- c. GC Column – mid-polarity capillary column (HP-5, 30 m, 0.25 mm i.d., 0.25 μ m film or equivalent)
- d. Carrier Gas - Helium, 99.99% (high purity)
- e. Sample holder - alloyed metal cups (Frontier or equivalent)
- f. Cleaning apparatus for sample holders (e.g., aluminum block, muffle furnace, small butane torch, sample cup inspector, sample cup holder)
- g. Polystyrene Pellets (Scientific Polymer Products, Inc. or equivalent)

- h. High Density Polyethylene Pellets (Scientific Polymer Products, Inc. or equivalent)
- i. Perfluorotributylamine (PFTBA, FC-43) (Agilent or equivalent)
- j. Stereo-microscope (~ 6 to ~ 50x) with appropriate lighting (annular ring light or fiber optic light)
- k. Scalpel with blades
- l. Wire probe
- m. Tweezers
- n. Glass microscope slides
- o. Analytical microbalance

4 Standards and Controls

4.1 Performance Verification Standards

4.1.1 Polystyrene Standard (Daily QA/QC Standard)

The polystyrene is used to assess daily operating performance, mass assignment, and continued integrity of the system. It can be purchased as a standard in pellet form. Prepare for analysis by cutting a polystyrene pellet to obtain a size that will provide an adequate signal. Place the polystyrene in the bottom of a sample cup.

4.1.2 Polyethylene Standard (Monthly QA/QC Standard)

The polyethylene is used to assess monthly operating performance, column selectivity, and continued integrity of the system. It can be purchased as a standard in pellet form. Prepare by cutting a polyethylene pellet to obtain a size that will provide an adequate signal. Place the polyethylene in the bottom of a sample cup.

4.2 PFTBA Tuning Solution

The PFTBA tuning solution is used for tuning the mass spectrometer and verifying mass calibration. It is supplied by the instrument manufacturer and does not expire. It is stored in a glass container attached to the MSD. Under normal conditions, this should not need to be refilled.

5 Sampling or Sample Selection

Not applicable.

6 Procedures

6.1 Daily Checks

The following steps will be performed daily. Enter the appropriate information in the QA/QC log.

- a. Perform a tune of the instrument. If Autotune (ATUNE) is selected, the mass spectrometer will tune itself using PFTBA. Evaluate the results using the 'Decision Criteria' section of this protocol. If the results are acceptable, print the tune file (ATUNE) when completed.
- b. Perform an analysis of a blank followed by a polystyrene standard prior to sample analysis. Open the appropriate instrument method, and verify the parameters as listed in the 'Instrumental Conditions' section of this protocol. Set up a sequence, load the autosampler with a blank and a sample vessel containing the polystyrene, and start the analysis. Evaluate the results using the 'Decision Criteria' section of this protocol. If the results are acceptable, print the TIC and mass spectra for the polystyrene as well as for the prior blank.
- c. If all requirements are within specification, prepare the documentation as outlined in the "General Instrument Maintenance Protocol." If any requirements fail, contact appropriate instrument support personnel.

6.2 Monthly Checks

The following steps will be performed monthly. Enter the appropriate information in the QA/QC log to indicate completion.

- a. Perform an analysis of a blank followed by the polyethylene standard. Open the appropriate instrument method, and verify the parameters as listed in the 'Instrumental Conditions' section of this protocol. Set up a sequence, load the autosampler with a blank and a sample vessel containing the polyethylene, and start the analysis. Evaluate the results using the 'Decision Criteria' section of this protocol. If the results are acceptable, print the TIC for the polyethylene as well as for the prior blank.
- b. If all requirements are within specification, prepare the documentation as outlined in the "General Instrument Maintenance Protocol." If any requirements fail, the IOSS Manager or appropriate instrument support personnel will determine the corrective action to be taken.

7 Instrumental Conditions

Refer to the “Pyrolysis-Gas Chromatography/Mass Spectrometry Analysis of Paints, Tapes, and Polymers” SOP for recommended instrument conditions.

8 Decision Criteria

8.1 Tune

Verify the results of the tune. Compare the results of the tune to previous tune results. Significant voltage increases or changes in the isotope ratios indicate the need to initiate corrective maintenance procedures. The following are typical ATUNE values for the MSD:

- a. PFTBA Tune: $m/z \pm 0.4$ for m/z 69, 219, and 502
- b. Peak width: 0.45-0.65
- c. Relative abundance: 69 greater than 50%
219 greater than 50%
502 greater than 1%

8.2 Polystyrene and Polyethylene

Verify the results.

- a. In order for the instrument to be considered in good operating condition, all components should generate well-resolved, Gaussian-shaped peaks with baseline separation.
- b. A SNR of 3:1 will be the minimum response necessary to consider a response a peak.
- c. There should be no significant unrelated peaks in the pyrogram.
- d. Ideally, the blank preceding the performance verification standard should not exhibit any chromatographic peaks greater than the CO₂ response; if extraneous peaks are present but explainable (e.g., siloxanes), this should be noted on the blank printout for technical review.
- e. The retention times of each component should be similar as compared to previous analyses (unless GC maintenance has been performed, such as column clipping or replacement).
- f. For polystyrene, check for the correct mass assignments in the mass spectrum, and compare the fragmentation patterns with previous analyses.

- Monomer ions - 50, 51, 77, 78, 103, and 104 (base peak).
- Dimer ions - 65, 91 (base peak), 104, 115, 117, 130, 193, and 208.
- Trimer ions - 91 (base peak), 115, 117, 194, 207, and 312.

g. For polyethylene, observe that there is baseline separation between the groupings of dialkenes, alkenes, and alkanes. Furthermore, compare with previous analyses.

9 Calculations

Not applicable.

10 Measurement Uncertainty

Not applicable.

11 Limitations

Not applicable.

12 Safety

Take standard precautions for the handling of all chemicals, reagents, and standards. Refer to the *FBI Laboratory Safety Manual* for the proper handling and disposal of all chemicals. Personal protective equipment should be used when handling any chemical and when performing any type of analysis. Many instrument components are held at temperatures of 250°C and higher, and areas of the pyrolysis autosampler reach temperatures in excess of 800°C. Precautions should be taken to prevent the contact of skin with heated surfaces and areas.

13 References

Manufacturer(s)'s Instrument Manuals for the specific models and accessories used.

"General Instrument Maintenance Protocol" (Inst 001) *Instrument Operation and Systems Support SOP Manual*.

"Gas Chromatograph General Maintenance Protocol" (Inst 002) *Instrument Operation and Systems Support SOP Manual*.

"Mass Spectrometer General Maintenance Protocol" (Inst 004) *Instrument Operation and Systems Support SOP Manual*.

“Pyrolysis-Gas Chromatography/Mass Spectrometry Analysis of Paints, Tapes, and Polymers”
(PPSU 201) *Paints and Polymers SOP Manual*.

FBI Laboratory Safety Manual.

Rev. #	Issue Date	History
4	03/26/15	Changed scope and principle to be non-instrument specific; edited equipment list in Section 3 to align with order in PPSU 201; edited Sections 4.1.1 and 4.1.2 to be inclusive of different sample intro methodologies for different instrument types; removed recording of disk space from Section 6.1 as well as save to disk instruction since program autosaves this info; changed reference for Decision Criteria in Section 6.2a to PPSU SOP 201. Removed sections 7.1-7.3 because the information is covered in PPSU SOP 201 for this technique; also changed "specific" to "recommended" in Section 7 since the parameters are a guide for use of two different instrument systems, no longer specific to one instrument type/brand. Minor grammatical editing throughout. Section 8.2c simplified language, 8.2d accounted for explainable extraneous peaks and 8.2e changed allowable deviation range for RT to align with other subunits. Updated references.
5	10/04/18	Updated Section 1 Scope to include disciplines/categories of testing. Removed all references to 'CDS' in Section 3. Updated sample placement in Sections 4.1.1 and 4.1.2. Updated to 'appropriate instrument support personnel' in Sections 6.1 c and 6.2 b. Updated Section 8.2 c & e to account for instrument variation and maintenance. Updated 'Instrument Operation and Systems Support' in Section 13 and header.

Approval

Redacted - Signatures on File

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